5.3.9.2   SETTING FILTER PACK AND SEALS

Silica sand was placed around the GeoProbe® screen to a height about 6 inches above the top of the screen. Granular bentonite and water were then added in two lifts of 3 inches, each individually hydrated with about two cups of distilled water before installing the next lift, followed by two 6-inch lifts and then as many 1-foot lifts as needed to reach up to 6-inches below the bottom of the next probe screen. Six inches of silica sand was placed on top of the seal prior to placing the next probe.

Separate tremmie pipes were used to convey the granular bentonite and water into the borehole below the bottom of the hollow stem augers while constructing the probe seals to prevent bridging within the augers. A weighted fiberglass measuring tape was used to confirm the depth intervals of all seals and sand-packs. The surface completions were 12-inch diameter, lockable-traffic rated casings with sufficient room to coil the tubes and valves and secure them inside. The northing and easting coordinates were surveyed relative to the state plane coordinate system by a professional surveyor licensed within the State of Ohio. Survey locations for the newly installed nested soil vapor wells were tied into previously established benchmarks at the site and Hooven. The horizontal accuracy for the nested soil vapor wells was established as +/- 0.1 foot. Installation logs are presented in Appendix B.

Nested soil vapor monitoring well VW-130 caved in after the installation of the 30-foot depth interval. The remainder of the shallower probes were installed in an adjacent borehole.

5.3.9.3   SEAL TESTS FOR EXISTING NESTS

All of the nested soil vapor monitoring wells have multiple probes within a single borehole, which makes it critical to confirm the competence of the seal between probes. Seal tests were conducted by drawing a vacuum of approximately 30 in-H_2O on a selected probe, and measuring the vacuum response at the probes immediately above and below. This test was repeated for each probe in sequence. None of the vacuum measurements showed immediate and significant vacuum, which would be diagnostic of a leaky seal. Therefore, all seals were considered to be competent and fit for sampling.

5.4   SOIL-GAS MONITORING

A general description of soil-gas monitoring procedures was provided in the Work Plan. Additional details are provided below. Sampling field forms are included in Appendix C.

Trihydro

5.4.1 STATIC PRESSURE/VACUUM MEASUREMENTS

A DP-Calc™ digital micro-manometer or Magnehelic gauge (0 to 0.25 in-H20) was connected to each sub-slab and near-slab soil-gas sampling point prior to pneumatic testing to measure static pressure or vacuum to assess whether there are any pressure gradients that might induce soil-gas flow. The measurements were recorded on the field monitoring forms (Appendix C).

5.4.2 PNEUMATIC TESTING

The gas permeability of geologic materials around the soil-gas probes or granular fill beneath the sub-slab sampling points was calculated by measuring the flow rate of soil-gas through the probe and the corresponding vacuum at flow rates low enough to minimize line losses (generally 0.2, 0.5 and 1.0 L/min, but in some cases, additional flow rates were tested). The gas permeability was calculated from these data and equations provided in Johnson et. al.(1990). The gas permeability values are useful for assessing whether there are depth intervals within the unsaturated zone that might provide preferential pathways or vapor barriers.

5.4.3 PURGING AND FIELD SCREENING

All soil-gas probes were purged prior to sampling using a dedicated 3-liter Tedlar® bag and lung box. Soil-gas collected into the Tedlar®bag was field-screened using a MiniRae 2000™ or Photovac 580™ photoionization detector (PID) and Landtech™ multigas $O_2/CO_2/CH_4$ meter. The dedicated Tedlar® bag was filled, screened, and then evacuated a minimum of three successive times to confirm field screening readings had stabilized prior to collecting a soil-gas sample for laboratory analysis.

The same protocol was used to sample the sub-slab probes and near-slab probes with the following additional steps. Helium was used as a tracer to ensure atmospheric air did not bias the sub-slab sample by leaking through the annular seal between the floor slab and probe. A shroud was placed around the ground surface of each sub-slab probe prior to sampling. Helium gas was added to the shroud through a small port. The concentration of helium in the shroud was recorded with a Mark 9822™ or Dielectric MGD2000™ portable helium detector to confirm that the shroud contained a minimum of 10% helium prior to purging. Soil-gas samples collected in the Tedlar® bag were also screened to confirm that the concentration of helium in the samples were less than 5% of the concentration in the shroud, verifying that the sample consists of at least 95% soil-gas prior to collection of the sample for laboratory analysis. If the soil-gas helium concentration exceeded 5% of the shroud concentration, this indicated an unacceptable leak and the sub-slab probe was re-sealed or replaced.

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5.4.4 SAMPLE COLLECTION, SHIPPING AND HANDLING

After field screening readings stabilized, a fourth and final 3-liter Tedlar® bag sample was filled and field screened to confirm consistency with previous readings. The Tedlar® bag was then attached (using compression fittings) directly to a certified 1-liter Summa canister with a 5-micron in-line filter. No flow controllers were used. Instead, the Summa canister valve was slowly opened to draw the sample from the Tedlar® bag, and closed such that some residual vacuum remained in the Summa canister, if possible (typically 1 in-Hg to 8 in-Hg). Summa canisters were then shipped to the laboratory under chain-of-custody control. Initial (before sample collection) and final (after sample collection but before shipping to the laboratory) vacuums of each Summa canister were recorded in the field notes and on the sample tag.

5.4.5 LABORATORY ANALYSIS

All soil vapor samples were analyzed by ATL. All sub-slab, near-slab and vapor nest Summa canisters were analyzed for VOCs using EPA method TO-15 for the full suite of analytes and a target reporting limit of 0.5 parts-per-billion by volume (ppbv). Analyses were also conducted for fixed gases (including O_2 and CO_2) by ASTM Method D 1945.

5.4.6 EQUIPMENT TEST FOR NAPHTHALENE

Naphthalene has a tendency to adsorb to surfaces, which might impart a bias on the results of soil-gas sampling and analysis, possibly including the inside of Tedlar® bags and Summa canisters. Therefore, an equipment check was performed to assess whether and to what extent this might be a concern. ATL provided a pressurized 6 L Summa canister spiked with 10 ppbv naphthalene. A 1-foot length of ¼-inch Nylaflo™ tubing was attached to the 6 L Summa™ canister by a compression fitting, and a 3 L Tedlar® bag was filled to a volume of 1 L. The contents of the bag were emptied to mimic the field screening procedure (see Section 6.4.3), in which Tedlar® bags are filled and emptied repeatedly prior to collection of a Summa canister sample. The Tedlar® bag was then re-filled following the same protocol three more times. The fourth Tedlar® bag was then attached directly to a certified 1-liter Summa canister with a 5-micron in-line filter using compression fittings. The Summa canister valve was slowly opened to draw the sample from the Tedlar® bag, and closed such that some residual vacuum remained in the Summa canister, if possible (typically 1 in-Hg to 8 in-Hg). Summa canisters were then shipped to the laboratory under chain-of-custody control. Initial (before sample collection) and final (after sample collection but before shipping to the laboratory) vacuums of each Summa canister were recorded in the field notes and on the sample tag. Both the 6 L standard

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canister and the 1-L sample canister were shipped under chain of custody to the laboratory and analyzed for naphthalene concentrations using EPA Method TO-15 in open scan mode for comparison to the initial 10 ppbv standard concentration to assess whether any negative bias might be imposed by the sampling procedure.

5.5 GROUNDWATER MONITORING WELLS

Nine additional groundwater monitoring wells (MW-121, MW-122, MW-124 through MW-130) were installed in order to more fully delineate the lateral extent of LNAPL/dissolved contaminant impacts beneath Hooven and if necessary to assist with forensics evaluation of potential indoor air contaminants and constituents detected in soil-gas that are associated with the petroleum hydrocarbon plume. Proposed groundwater monitoring well MW-123 could not be installed due to access limitations. Proposed groundwater monitoring well MW-131 was not installed due to a very thin sediment cover on the Ordovician bedrock. Also a groundwater table was not encountered in the thin valley alluvium. The borehole was abandoned per Ohio EPA and U.S. EPA requirements. Figure 2a presents the location of the newly installed and existing monitoring wells located in Hooven.

5.5.1 SOIL BORING INSTALLATION

Prior to installation of the soil borings, Chevron obtained necessary permits from the Hamilton County Engineer's Office and access agreements from Whitewater Township and private property owners. Underground utilities were clearly identified via notification to Ohio Utilities Protection Service (OUPS) prior to installation of each soil boring. Soil borings were installed via direct push drilling technique utilizing an AMS 9630 Power Probe.

5.5.2 SOIL SAMPLING PROCEDURES

A 2.75-inch diameter soil boring was continuously cored using a 5-foot continuous core sampler to the top of groundwater at each proposed monitoring well location. Soil samples were collected in accordance with the following procedures:

- Field team personnel wearing disposable nitrile gloves extracted the samples from the continuous sampler. Soil from the uppermost section of the sampler was discarded, as it may have contained borehole slough;

- An aliquot of the soil from each 5-foot interval was placed in a re-sealable plastic bag and the headspace was monitored for total organic vapors;

- Soil samples with visible staining or total organic vapor concentrations greater than 50 parts per million were collected for laboratory analysis;

- Soil samples targeted for geotechnical analysis were identified and the desired interval isolated; and

- The remaining soil from each borehole was used by the field geologist to produce a lithologic log in general accordance with ASTM standards. Additional information, such as odors, discoloration, artificial/non-native debris, and observations pertaining to potential petroleum hydrocarbon impacts were noted on the lithology logs. Lithology logs for each of the soil borings are included in Appendix B.

5.5.3   ORGANIC VAPOR SCREENING

Soil samples were screened for total organic vapor using a Thermo Environmental 580EZ, Thermo Environmental 580S2, or MiniRae 2000 photoionization detector (PID). The PID was calibrated daily, in accordance with the manufacturer's guidelines, to a factory-prepared 100 parts per million isobutylene standard. Each sample was allowed to equilibrate to room temperature before screening for total organic vapors. The total organic vapor measurement for each five foot interval was recorded on the lithology log (Appendix B) in parts per million, relative to the calibration standard. The accuracy of the PID was checked at the conclusion of each day by screening the PID against the 100 parts per million isobutylene standard.

5.5.4   SAMPLE COLLECTION FOR SOIL QUALITY ANALYSIS

Soil samples were collected from each borehole for laboratory analysis based on the field screening results and physical observations. The samples were collected and analyzed in general accordance with the Test Methods for Evaluating Solid Waste, EPA, SW-846 (SW-846, Revision 3, June 1997). Any soil samples with visible staining or total organic vapor concentrations greater than 50 parts per million were collected in a 12-ounce wide glass jar with no preservative and submitted for analysis of semivolatile organic constituents (SVOCs) via EPA Method 8270C.

The lids on each sample container were tightly secured and the sample label filled out completely including sample identification, sample interval, date and time of collection, project name, client name, field personnel initials, requested analyses, and preservation methods. The sample containers were placed on ice and proper custody maintained. Glass containers were protected against breakage during transport to the laboratory. A chain-of-custody form and temperature blank were submitted with each sample cooler shipped to the laboratory. The soil samples were submitted to Lancaster Laboratories, Inc. located in Lancaster, Pennsylvania.

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5.5.5 SAMPLE COLLECTION FOR GEOTECHNICAL ANALYSES

Field team personnel extracted the samples within 5-foot acetate liners from the continuous sampler. Soil samples targeted for geotechnical analyses were isolated and remained intact. The acetate liner containing the desired soil interval was then cut and ends capped to prevent agitation during shipment. Samples that were collected solely for particle size distribution were collected within a 4-ounce wide-mouth glass jar with no preservative. The sample identification, date and time of collection, and sample interval were clearly marked on the of the geotechnical sample.

Soil samples from selected borings were submitted for geotechnical analysis for Atterberg limits (ASA1 Method 31-1), bulk density (ASA1 Method 30-2), moisture content (ASTM Method D2216), total porosity (ASA1 Method 21-2.2), and/or particle size distribution (ASTM Method D422). Proper sample custody was maintained during collection and shipment of the geotechnical samples. Glass containers were protected against breakage during transport to the laboratory. A chain-of-custody form accompanied the samples to the laboratory. Geotechnical samples were submitted to Colorado Analytical Laboratories, Inc. located in Brighton, Colorado

5.5.6 DECONTAMINATION PROCEDURES

Before arriving at the site, the drill rig, tools, and accessories were thoroughly decontaminated with a pressure washer/steam cleaner. Down-hole equipment was decontaminated between borings at the Chevron Cincinnati Facility using a hot water pressure washer.

Soil sampling equipment was decontaminated between sample intervals using a phosphate-free detergent wash, and a potable water rinse followed by a distilled water rinse. Soil cuttings were containerized and transported to the Chevron Cincinnati Facility for appropriate handling and disposal. Decontamination fluids were collected and disposed of into the facility wastewater treatment facility.

5.5.7 GROUNDWATER MONITORING WELL CONSTRUCTION

After advancement of each soil boring to the total depth, the borehole was over-drilled to an 8-inch diameter utilizing an Acker SoilMax hollow stem auger drilling rig. The boring was advanced from ground surface to approximately 10 feet below the groundwater table. Following completion of the boring to total depth, a groundwater monitoring well was installed using 15 feet of two-inch diameter, 0.010-inch factory-slotted polyvinyl chloride (PVC) pipe inserted through the augers. PVC flush-threaded blank casing was installed from the top of the screened interval to

Trihydro

approximately 0.5-ft-bgs. Well screen and riser pipe remained in plastic until use, and were handled by field personnel wearing disposable nitrile gloves.

A filter pack consisting of clean, graded, 10/20 silica sand was placed within the borehole annulus to a minimum depth of 2 feet above the top of the screened interval. An annular seal consisting of approximately 2 feet of hydrated benseal granular bentonite was placed above the filter pack. Portland cement grout (95% cement, 5% powdered bentonite) was then placed above the seal to approximately 1 ft-bgs. The groundwater monitoring wells were completed beneath ground surface within a traffic-rated flush mounted vault. Groundwater monitoring wells were primarily installed within the main roads and alleys in Hooven and were completed to match the grade and composition of the road surface. Construction diagrams for each of the groundwater monitoring wells installed in Hooven during the vapor investigation are provided in Appendix B.

Following installation of the nine groundwater monitoring wells in Hooven, top of casing and surface elevations, as well as, northing and easting coordinates were surveyed relative to mean sea level and the state plane coordinate system by a professional surveyor licensed within the State of Ohio. Survey locations for the groundwater monitoring wells were tied into previously established benchmarks at the facility and Hooven. The horizontal accuracy for the groundwater monitoring wells was established as +/- 0.1 foot and the vertical accuracy was +/- 0.01 foot. The well designation and measuring point were clearly labeled inside each of the flush-mounted vaults.

5.5.8   GROUNDWATER MONITORING WELL DEVELOPMENT PROCEDURES

A minimum of 24-hours following construction, the groundwater monitoring wells were developed to remove accumulated sediments from the boring and well casing which may have been introduced during drilling and well construction activities. Newly installed wells were developed by mechanically surging the well followed by over-pumping until stabilization of water quality parameters, or until a minimum of 10 casing volumes of water were removed. Monitoring well MW-130 was installed within a lower permeability zone, and as a result, the well was developed until bailed dry, a minimum of two times.

Prior to mechanical surging, a minimum of one well volume was evacuated from the well to prevent sand locking of the surge tool. Surging consisted of forcing water into and out of the formation using a surge block. The surging action was relatively gentle to avoid collapsing the well screen or slumping formation material into the screen. Surging was concentrated over 5 foot intervals starting at the top of the screen to avoid sand locking the surge block.

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Groundwater in the well was then pumped at a rate exceeding that of natural recharge (over-pumping) until stabilization of pH, temperature, specific conductivity, dissolved oxygen, oxygen-reduction potential, and turbidity values (field parameters), as measured at regular intervals utilizing an In-Situ Troll 9000 or Horiba U-22XD multi-parameter meter throughout the evacuation process. The multi-parameter water quality meter was calibrated daily, in accordance with the manufacturer's guidelines, using a factory-prepared calibration standard. The volume evacuated from each well, field parameters, and physical characteristics of the purge water (color, relative turbidity, sediments, etc.) were recorded during regular intervals throughout development activities. Well development forms for each of the newly installed monitoring wells are included in Appendix B.

Development fluids were collected and disposed of into Chevron's facility wastewater treatment facility. A well log and drilling report (ODNR Form 7802.03) was submitted to the Ohio Department of Natural Resources documenting the well construction and development details for each of the new monitoring wells installed in Hooven.

5.5.9 FLUID LEVEL GAUGING PROCEDURES

Fluid levels within monitoring wells MW-81S, MW-93S, MW-96S, MW-99S, MW-100, MW-113, MW-121, MW-122, MW-124 through MW-130 were measured by field personnel wearing disposable nitrile gloves. Fluid level measurements were conducted using a Solonist 122 interface meter accurate to 0.01-feet. The measurements were completed from the pre-marked (surveyed) measuring point on the north side of the well casing. Manufacturer's instructions were followed to ensure proper care of the fluid level probe. The exposed portion of the tape and the probe were decontaminated before performing measurements at each monitoring well.

5.5.10 WELL PURGING USING LOW FLOW PROTOCOLS

Newly installed monitoring wells MW-121, MW-122, MW-124 through MW-129, as well as existing monitoring wells MW-81S, MW-81D, MW-95S, MW-95D, MW-100, MW-101, and MW-113 were purged and sampled following low flow protocols. Low flow sampling conformed to EPA recommended procedures (Puls et. al., 1995). Monitoring well MW-130 could not be sampled utilizing low flow procedures as the well was installed within a lower permeability zone. Monitoring well MW-130 was bailed dry and samples were collected following sufficient recharge of groundwater into the well.

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Dedicated or portable submersible pumps were installed so that the pump intake height was located in the middle or slightly above the middle of the saturated portion of the screen. The flow rate was maintained between 0.1 and 0.5 liters per minute to minimize drawdown and to avoid undue pressure, temperature, or physical disturbances to groundwater over the sampling interval. The water level and field parameters were recorded over successive time intervals using a Solonist 122 interface meter and an In-Situ Troll 9000 or Horiba U-22XD multi-parameter meter. The multi-parameter water quality meter was calibrated daily, in accordance with the manufacturer's guidelines, using a factory-prepared calibration standard. In general, the following stabilization criteria were achieved over three successive readings before collecting groundwater samples:

- pH ± 0.5;

- Specific conductivity ± 5%;

- Turbidity ± 10% or <10 nephelometric turbidity units;

- Dissolved Oxygen (DO) ± 10%; and

- Oxygen Reduction Potential (ORP) ± 10%

Groundwater sampling forms were maintained for each of the monitoring wells sampled during the Hooven Vapor Investigation and are included as Appendix C. Portable submersible pumps and groundwater sampling equipment was decontaminated between monitoring wells in the following manner:

- External surfaces were brushed free of loose material, washed with a phosphate free solution and potable water, and rinsed with distilled water; and

- Internal surfaces were cleaned by placing the pump in a clean bucket containing a phosphate-free decontamination solution and allowing the pump to operate for several minutes to circulate the decontamination solution through the impellers and pump housing. The pump was then rinsed by circulating with potable water, followed by a distilled water rinse.

Decontamination fluids and purge water were collected and disposed of into the facility wastewater treatment facility.

5.5.11 GROUNDWATER SAMPLING PROCEDURES

Groundwater samples were collected upon completion of purging by field personnel wearing disposable nitrile gloves to prevent cross contamination of groundwater samples. Sample agitation was minimized during sampling activities and groundwater was transferred directly from the pump discharge tubing into the sample containers; intermediary containers were not used for sample collection. Preservatives were added to each sample bottle in the laboratory prior to shipment to the site.

5.5.12 SAMPLE COLLECTION FOR GROUNDWATER QUALITY ANALYSIS

The samples were collected and analyzed in general accordance with the Test Methods for Evaluating Solid Waste, EPA, SW-846 (SW-846, Revision 3, June 1997). Groundwater samples were submitted for analysis VOCs via EPA Method 8260B, SVOCs via EPA Method 8270C, and total/dissolved metals via EPA Method 6020.

The lids on each sample container were tightly secured and the sample label filled out completely including sample identification, date and time of collection, project name, client name, field personnel initials, requested analyses, and preservation methods. The sample containers were placed on ice and proper custody maintained. Glass containers were protected against breakage during transport to the laboratory.

Duplicate groundwater samples were collected at a rate of one per 10 primary samples and analyzed for the full analytical suite. Matrix spike/matrix spike duplicate (MS/MSD) samples and equipment blanks were collected at a rate of one per 20 primary samples and analyzed for the full analytical suite. A chain-of-custody form, temperature blank, and trip blank (to be analyzed for VOCs via EPA Method 8260B) were included with each sample cooler shipped to the laboratory. The groundwater samples were submitted to Lancaster Laboratories, Inc. located in Lancaster, Pennsylvania.

5.6 OUTDOOR AIR MONITORING

In general, outdoor ambient air samples were collected from three locations on each day soil-gas sampling was conducted. One sample location (OA-3) was in the general vicinity of the sampling activities (20 to 100 feet away) and typically was transported with the sampling crew's vehicle. The sample valve was closed during transport. The other two outdoor ambient air samples were stationed in the backyards of HOO8 and CHI2. Locations of the fixed outdoor air sample stations are shown in Figure 2b.

Trihydro

5.6.1 SAMPLING AND ANALYSIS

Each sample was collected using a 6-liter Summa canister suspended 5 feet above ground, using a flow-controller calibrated to collect the sample over an 8-hour period. Collected samples were submitted to ATL for analysis of VOCs using modified method TO-15 which yielded reporting limits approximately one fifth of that used in standard TO-15 analyses.

5.6.2 METEOROLOGICAL DATA

A full scale weather monitoring station, located at the Chevron Cincinnati Facility scale house, was utilized to acquire weather data throughout the investigation. Meteorological data, including ambient temperature, barometric pressure, rain fall, wind speed, and wind direction, was automatically logged on 10-minute intervals during sampling activities. Graphical representation of the meteorological data is provided as Appendix D.

5.7 DATA VALIDATION METHODS

This section describes the methods used for data validation of vapor, soil, groundwater and LNAPL samples. Data were validated to evaluate if they were of sufficient quality to meet the requirements of the work plan for pathway evaluation/risk assessment.

Validation of laboratory results was performed according to EPA data validation procedures (EPA, 1999 and 2002c) modified as needed to accommodate the specific analytical methods used. The principles of precision, accuracy, representativeness, completeness and comparability (PARCC) were followed:

- Precision

    - a measure of the variability of individual sample measurements

    - evaluated by comparison of results of laboratory duplicate and field replicate analyses using relative percent difference (RPD)

- Accuracy

    - a measure of the analytical bias (difference between the actual sample analyte value and the measured sample analyte value)

    - evaluated by analyzing samples of known concentration (initial and continuing calibration, surrogate

compounds added to samples during analysis, laboratory control samples, MS/MSD samples) and calculating the percent recovery (%R)

- Representativeness

  - a measure of the degree to which the data set accurately reproduces the characteristics of the population

  - sampling locations must be chosen to adequately represent the population

  - evaluated in two steps:

    - in the field -- by examining field parameters collected during sample purging. This step is particularly important when validating vapor samples because atmospheric air may be introduced into a sample through a leak in the sampling train that is directly unobservable but purging parameters may provide indications of leaks at the time of sample collection.

    - in the laboratory -- by evaluating instrument performance checks, initial and continuing calibration, laboratory blanks, internal standards, sample homogenization

- Completeness

  - a measure of the amount of data collected, analyzed and validated compared to the amount specified in the sampling plan

  - evaluated by calculating the percentage of the number of valid data points that should have been collected

- Comparability

  - a qualitative measure of the confidence with which one data set can be compared against another

  - ensured at the time of sampling plan development by specifying sampling methods that are consistent with those of other data sets that are to be comparable

  - evaluated during data validation by checking for consistency in analytical process (e.g., correct method used for all analysis, same analytes analyzed for, same units reported, holding times were met, detection limits are comparable).

Trihydro

The following qualifiers were added to data during the data validation process:

- U – detected in trip blank, therefore value changed to non detect;

- J – value is estimated and should be used with caution; and

- R – value has been rejected and should not be used.

Data validation protocols were followed when adding data qualifiers; however, data qualifiers were occasionally added based on professional judgment. Results are reported in Section 6.7.

GeoSyntec and Trihydro performed the data validation as follows:

- Vapor Data – GeoSyntec and Trihydro validated 23 and 29 sample delivery groups (SDGs), respectively. A Tier III validation was performed which included a full review and evaluation (including calculation checks) of a Level IV package, including all data summaries, individual sample results, initial and continuing calibration, instrument performance checks and all raw data. Chain-of-custody forms, sample holding times, quantitation limits and results of field QA/QC sample analyses were also evaluated

- Soil, Groundwater and LNAPL Data – GeoSyntec validated three soil SDGs and one combined groundwater and LNAPL SDG. A Tier II validation was performed from Level II data deliverables and included evaluation of sample results and quality assurance sample results.

As an additional measure of QA/QC, five vapor SDGs and one soil SDG were validated by both GeoSyntec and Trihydro to ensure comparable data validation procedures were followed.

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6.0 RESULTS

Due to the large volume of data collected during this investigation, the data are summarized in appendices and described briefly in this section. Summary tables of analytical data were compiled from a database and are included in the report appendices, by media, along with laboratory data sheets. Field documentation is also included in appendices.

6.1 BUILDING SURVEY DATA

The results of the occupied dwelling questionnaires indicated that there were two principal foundation construction types of interest among buildings and residences in Hooven: 1) full basement with concrete pad, and 2) partial basement with dirt crawlspace. It should be noted that trailer-style homes and slab on grade homes were not targeted for participation in the questionnaire. Questionnaire results indicated the predominant fuel source for indoor space heating was fuel oil. Fuel oil tanks were commonly housed in the basement and filled via a port passing through the exterior basement wall. Many Hooven residents indicated that smoking occurred in the home. At the time the questionnaires were administered, no sanitary sewer existed in Hooven. Accordingly, all residents completing the questionnaire indicated their dwelling had a septic tank and/or leach bed. Other potential secondary sources observed included lawn mowers, gas cans, and paint. Copies of all questionnaires appear in Appendix A.

6.2 GEOLOGY/HYDROGEOLOGY

The March-May 2005 drilling in Hooven has resulted in confirmation of previous characterizations of the geology and hydrogeology (e.g., CT Cincinnati GW Task Force, 2001 and CT Cincinnati GW Task Force, 2003). Borehole logs (Appendix B) have provided data for a generalized description of the surficial aquifer. Geologic materials properties tests (Appendix E) and pneumatic testing of soil-gas probes (Appendix C) provided specific information to support modeling, as needed.

6.2.1 SITE GEOLOGY

Sediment described in deep borings was grouped into four dominant categories: 1) sand and gravel, interbedded to massive; 2) gravel and cobbles, massive or interbedded with sand and/or silts; 3) predominantly sand with sparse gravels; and 4) silt or silt and clay with fine sand. A cross section location map is included as Figure 3 and the related cross sections are included as figures 4, 5, and 6. The vast bulk of the sediment volume under Hooven is comprised of the first three categories of coarse material. The finer beds are confined largely to the western third of town at the

Trihydro

surface, in a layer up to ten feet thick. Boring logs indicate that the thickness of sediment on top of the Ordovician bedrock is roughly 100 feet in the eastern and central portions of town but thins significantly to the west (figures 3, 4). Though a well was not installed, the boring log for MW-131, indicates that bedrock elevation rises and the sediment cover thins to less than 20 feet in the westernmost portion of town. Water was not encountered at the bottom of the borehole at MW-131.

The fine-grained surface layer acts as an aquiclude such that after rain events in April, some near-slab sampling points installed in the clay were observed to contain water. Some sub-slab sampling points installed in homes whose basements were excavated into this clay layer became flowing artesian wells upon installation apparently because the engineered gravel fill under some house footprints had become saturated during rainfall events preceding the sampling.

6.2.2   GEOLOGIC MATERIAL PROPERTIES AND CHEMICAL ANALYSES

Soil samples collected from various depths in near-slab and nested soil-gas probes were submitted for laboratory chemical analyses of SVOCs, metals, and geotechnical analysis for Atterberg limits, bulk density, moisture content, total porosity, and/or particle size distribution (Appendix E).

6.2.3   PNEUMATIC TESTING RESULTS

Soil permeability to gas was calculated from pneumatic tests performed on each soil-gas probe. Sub-slab values were highest, averaging 5.E-10 m^2. These results are consistent with a coarse, engineered sub-slab fill having relatively high permeability. Near-slab sediment averaged roughly an order of magnitude lower, and nested probes ranged over one and one half orders of magnitude, falling to nearly 1.E-12 m^2 at the bottom (Appendix C). These results are consistent with natural sediment that increases compaction with depth and concurrently loses permeability. With the exception of shallow clayey soil located on the western portion of Hooven, the remainder of the geologic materials were relatively uniform.

6.3   SOURCE CHARACTERIZATION DATA

A single sample of LNAPL, from MW-96S, was obtained for laboratory analysis. Insufficient volume of LNAPL was present in well MW-99 for laboratory analysis, however even an imperceptible sheen can measurably affect analytical results. The results of the LNAPL sample analysis from MW-96S are included as Appendix F. Thirteen volatile constituents (including naphthalene) and two semivolatile constituents (also including naphthalene) were identified. In

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order of decreasing concentration, the detected constituents were 1,2,4-trimethylbenzene, m&p xylenes, n-hexane, 2-methyl naphthalene, 1,3,5-trimethylbenzene, ethylbenzene, n-propyl benzene, naphthalene, n-butyl benzene, isopropylbenzene, sec-butyl benzene, o-xylene and benzene. The simulated distillation analysis (modified ASTM D3328) indicated a carbon range distribution most similar to that of partially evaporated gasoline. Minor amounts of longer chained hydrocarbons (>C14) were also identified in the chromatogram. These results are consistent with previous characterizations of LNAPL under the facility and beneath Hooven (e.g., Duke, 2004).

Vapor phase characterization of SVOCs was conducted on the existing nested soil vapor wells over the plume (VW-93, VW-96, and VW-99) at a probe depth immediately above the groundwater table. The analytical results for the SVOC vapor sampling (including TICs) are included in Appendix F. The analytical reports and data validation reports are included as Appendix F. The only constituent positively identified in the three samples, was 2-methyl naphthalene. It was detected at a concentration of 5.6 $\mu g/m^3$ in the sample from the 55 foot interval in VW-99; it was not detected in the other samples. Several TICs were reported by the laboratory.

6.4   GROUNDWATER MONITORING DATA

As described in the Work Plan, shallow groundwater wells were sampled to better define the extent of LNAPL and dissolved petroleum hydrocarbons in Hooven. Nine new wells and seven previously existing wells were sampled. The locations of the groundwater wells are shown on Figure 2a. Tabulated analytical results are presented on Table 3. The laboratory data and data validation summaries for the groundwater samples collected in April-May 2005 are included in Appendix G. Field documentation for the groundwater sampling is included in Appendix C.

6.4.1   GROUNDWATER POTENTIOMETRIC SURFACE

Fluid level measurements were used to generate the potentiometric surface map, presented in Figure 7. The fluid level measurements were gauged and recorded electronically in the field with a field personal digital assistant (PDA) and directly uploaded into a database. Figure 7, which indicates the groundwater measured elevation data, shows groundwater flow generally to the south. This is consistent with regional flow directions presented in previous reports (ESE, 1999; CT Cincinnati GW Task Force, 2003). The new wells installed in the west and central portion of town (i.e., MW-124, MW-129, and MW-130) provide additional control on groundwater flow in this area, relative to previous monitoring events. The southerly flow direction in the eastern portion of town, and the easterly flow component in the central portion of town are also consistent with the observed orientation of the LNAPL/dissolved contaminant plume (Figure 8), and the limited encroachment of the plume into the town. Monitoring well MW-130 was not used to create the potentiometric surface map because it is not believed to be representative of the

Trihydro

potentiometric surface. Rather, the significantly higher fluid level elevation measured in this well in concert with the known geology, provides evidence that recent rainfall had infiltrated the surface sediment and was traveling along the boundary with the Ordovician bedrock towards the regional water table.

6.4.2   FIELD PARAMETERS

The field parameter data are included on the groundwater field forms in Appendix C. The parameters pH, specific conductivity, turbidity, DO, and ORP were monitored during well purging and immediately prior to sample collection. The primary purpose of monitoring field parameters is to document their stabilization to and collection of representative groundwater. The field parameter results have not been used in evaluations of the vapor intrusion pathway.

6.4.3   GROUNDWATER SAMPLING RESULTS

The groundwater analytical results are summarized on Table 3 and on Figure 8. The analytical reports and data validation reports are included as Appendix G. Each of the constituents that had been identified in the LNAPL sample was also detected in one or more groundwater samples. Additionally, the volatile constituents cyclohexane, acetone and 2-butanone were reported in one or more groundwater samples. Cyclohexane had not been on the reporting list for the LNAPL sample. However, it is a possible component of gasoline. Acetone and 2-butanone were evaluated in the LNAPL sample and were not detected; these constituents are common laboratory contaminants and are not likely to be components of gasoline.

Additional SVOCs identified in one or more groundwater samples included 1-methylnaphthalene and indene. Estimated concentrations, below the practical quantitation limit (PQL), of the compounds 2-4 dimethyl phenol, 4-methyl phenol, Bis(2-ethylhexyl) phthalate, and phenanthrene were identified in one or more groundwater samples, and were qualified by the laboratory with a "J." Of these, Bis(2-ethylhexyl) phthalate is a common laboratory contaminant and not likely to be a component of gasoline. Several additional SVOCs, including anthracene, benzo(a)anthracene, benzo(a)pyrene, chrysene, 6-methyl chrysene, di-n-octyl phthalate, fluoranthene and pyrene were identified, generally at concentrations below the PQL, in the groundwater sample from MW-96S. Of these, di-n-octyl phthalate is a common laboratory contaminant, and not likely to be a component of gasoline. The detection of the other SVOCs in this particular sample is likely due to entrainment of minute amounts of LNAPL in the sample. In fact, the purpose for collecting the sample was to identify constituents in the LNAPL, but insufficient LNAPL was present for analysis.

Trihydro

6.5 SOIL-GAS MONITORING DATA

The soil-gas monitoring data includes results from the sub-slab probes, near-slab probes and nested soil vapor wells. Sampling point locations are shown on figures 2a and 2b. Sampling and purging data is included in Appendix C. Summary tables of analytical data are provided on tables 4 through 6. Analytical laboratory reports and data validation reports included in Appendix H.

6.5.1 SOIL-GAS PERMEABILITY DATA

The monitoring data and calculated permeability values are shown on the summary tables in Appendix C for nested wells, near-slab probes and sub-slab probes. Soil-gas permeability testing generally showed similar results for all nested wells and near-slab probes, with specific capacities (flow rate per unit of vacuum applied) ranging from 0.5 to 5 liters per minute per inch of water column (L/min/in-H_2O). The resulting permeability values are generally in the range of 1.E-10 to 1.E-11 m^2, which are typical values for sand or coarse sand. There are notable exceptions in shallow probes in the western end of Hooven, where the shallow geologic materials are much less permeable and in some cases contained water from recent rainfall events that made pneumatic testing impracticable in some cases.

Sub-slab permeabilities were generally higher than near-slab or nested well measurements, which is to be expected, because granular fill materials are typically placed beneath floor slabs for structural reasons, and they are usually highly permeable materials. Some of the sub-slab probes in the eastern end of Hooven were wet, which indicated that recent rainfall was accumulating in the granular materials surrounding the floor slab and basement walls. Sample locations where water was encountered during pneumatic testing do not have calculated gas permeabilities.

6.5.2 STATIC VACUUM/PRESSURE DATA

A majority of the sub-slab, near-slab and nested soil vapor probes showed no significant static pressure or vacuum during initial measurement prior to pneumatic testing. Probes that filled with recent rainwater showed larger positive pressures in some locations; however, this is not considered representative of soil-gas pressure gradients. In general, initial static pressure or vacuum was in the range of 0 to 0.02 inches of water for sub-slab probes, near-slab probes and nested soil vapor wells, which is in the range that can be produced from wind and barometric pressure.

6.5.3 VOC SAMPLING RESULTS

Summary tables 4 through 6 provide the results of analysis of soil-gas samples from the sub-slab probes, near-slab

Trihydro

probes, and nested soil vapor wells, respectively. Copies of laboratory analytical reports and data validation reports are contained in Appendix H. The VOC data are concluded to be representative, of known and acceptable accuracy and precision, and suitable for use in addressing the objectives of this vapor intrusion assessment.

The collection of representative samples from HOO7-SS1/SS2, HOO10-SS1/SS2, HOO13-SS1/SS2, and HOO14-SS1/SS2 was not possible due to water encountered during sampling and low permeability beneath the slab. These locations are all located on the far west end of Hooven.

Nested soil vapor monitoring well locations VW-96 (60 ft-bgs) and VW-99 (60 ft-bgs) could not be sampled because the probe depth was below the water table. This was confirmed with water level measurements at nearby groundwater monitoring wells or by pneumatic testing.

The data from the nested soil vapor monitoring wells show that deep soil-gas samples in locations above the LNAPL/dissolved contaminant plume are elevated, but the concentrations decrease to negligible levels by depths of about 30 ft-bgs. Shallower samples have low concentrations of some VOCs, many of which are not gasoline constituents and are therefore not facility-related. The shallow concentrations are generally consistent with concentrations expected from background sources.

Data from the nested soil vapor monitoring wells were compared to soil-gas screening levels in Table 3b-SG of the OSWER Draft VI Guidance, as shown on figures 16 through 18. Samples in the depth interval from about 20 to about 40 ft-bgs were lower than the screening levels, which indicates that subsurface vapors attenuate by these depths, do not reach ground surface, and cannot migrate into overlying buildings. Therefore, the primary conclusion of this investigation is that the vapor intrusion pathway is incomplete at this site. In accordance with the OSWER Draft VI Guidance, if vapor concentrations do not exceed the screening concentrations, no further assessment is necessary. Nevertheless, additional scientific evidence is provided to increase the confidence in the incomplete pathway determination.

Shallow soil-gas concentrations (sub-slab and near-slab data) were detected at low levels and similar frequencies inside and outside of the LNAPL/dissolved contaminant plume and were generally consistent with background concentrations, as shown on Table 7. The background concentrations were taken from a report by the New York State Department of Health (NYDOH, 2005), in which samples were collected from inside homes heated with fuel oil, as a means of assessing background indoor air petroleum hydrocarbon concentrations. The distribution of detected

Trihydro

constituents in the shallow soil-gas does not spatially correspond to the footprint of the LNAPL/dissolved contaminant plume. Therefore, there is no indication that facility-related petroleum hydrocarbon sources at or near the groundwater table have any impact on shallow soil-gas concentrations.

6.5.3.1   NAPHTHALENE STANDARD TESTING DATA

Naphthalene equipment test data confirmed a concentration of 9.8 ppbv in the original Summa canister that was spiked with 10 ppbv naphthalene. This indicates that the laboratory is able to effectively remove naphthalene from Summa canisters prior to analysis and adsorption to the interior surface of the Summa canister does not pose any significant concentration bias.

A concentration of 5.1 ppbv naphthalene was detected in the sample collected from the Tedlar® bag, indicating that sample collection through a Tedlar® bag may impart a low bias of up to 2-fold for naphthalene, and similar molecular-weight compounds. Soil-gas detection limits for naphthalene (average of approximately 23 $\mu g/m^3$) were much lower than concentrations that could pose a risk via vapor intrusion (300 $\mu g/m^3$ Table 2b, OSWER Draft VI Guidance). Therefore, a negative bias of a factor of only two is not considered significant and the naphthalene data are fit for the purpose of evaluating the vapor intrusion pathway. Naphthalene was not detected in any samples (from deep nested vapor monitoring wells) that monitor the vapor intrusion pathway.

6.5.4 O_2/CO_2 RESULTS

O_2 and CO_2 were measured during soil-gas purging and sampling to determine that both steady state conditions had been achieved prior to the collection of a sample for laboratory analysis and to determine a trend of biodegradation with depth. Field screening data indicated that O_2 and CO_2 measurement were stable for sub-slab probes, near-slab probes and nested soil vapor wells. Field data is included in Appendix C.

Laboratory analysis of soil-gas samples for fixed gases including O_2 and CO_2 via ASTM-D-1945 document the vertical profile of O_2 and CO_2 concentrations in the study area, as shown in figures 9 to 15. These data show classic profiles of decreasing O_2 and increasing CO_2 with depth in locations over the LNAPL/dissolved contaminant plume, indicative of aerobic degradation of petroleum hydrocarbon vapors in the unsaturated zone. In areas outside the plume, the profiles do not show significant microbial activity. Analytical results are summarized on tables 4 through 6 and analytical laboratory reports are presented in Appendix H.

Trihydro

6.6   OUTDOOR AIR MONITORING

The outdoor air monitoring data includes results from the three sampling stations and meteorological data collected at the weather station at the former refinery. The locations of the sampling stations are shown on Figure 2b. A summary of the analytical data is provided on Table 8. Analytical laboratory data and data validation reports are included as Appendix I.

6.6.1   SAMPLING RESULTS

Both potentially gasoline and non-gasoline related constituents were detected at low concentrations in the outdoor air samples. Benzene, toluene, m,p xylenes, ethanol, dichlorodifluoromethane, and trichlorofluoromethane were detected in more than half the samples. Acetone was detected in every sample. Detection frequencies were similar inside and outside of the LNAPL/dissolved contaminant plume. Detected concentrations were generally within the range of background ambient air data from published studies (NYDOH, 2005). Outdoor air sample analyses reported exceedences of indoor air screening levels provided in the OSWER Draft VI Guidance, Table 2b for three compounds:

- four samples exceeded the benzene screening level

- eight samples exceeded the 1,3-butadiene screening level; and

- one sample exceeded the 1,2,4-Trimethylbenzene screening level.

6.6.2   METEOROLOGICAL DATA

During the period of sampling activities ambient temperatures oscillated daily with mean values ranging from 40 to 70° F, multiple rain events with associated drops in barometric pressure were recorded, and northerly to northeasterly winds predominated (the Chevron facility lies due east of Hooven, Ohio) at an average speed of 5.4 mph. Graphical representation of the meteorological data is provided in Appendix D.

6.7   DATA VALIDATION SUMMARY

This section presents a summary of the data validation. The data were found to be of suitable quality to meet the project objective of investigating the vapor migration pathway. A large and comprehensive data set was collected. The total number of individual sample events (including sub-slab, near-slab, and nested well soil-gas and outdoor air sample locations/dates) was 286 and the total number of valid samples was 285. Therefore, the data set is essentially 100% complete. In addition, approximately 2% of the data were qualified by the data validators as estimated. These data are

still useful for qualitative purposes. Given the large number of samples collected, this has negligible effect on the utility of the data set. Results of data validation for each SDG are presented in Appendices E through I.

6.7.1 CERTIFICATION OF SUMMA CANISTERS

In a letter dated June 16, 2005, ATL provided the results of their canister certification process for the time period of the Hooven Subsurface Vapor Investigation. The letter is included in Appendix H. The canister certification process is performed by the laboratory to monitor and evaluate the effectiveness to which canisters are cleaned prior to shipment to the field for sampling. The laboratory reported an 86% success rate (within acceptable limits) which indicates that a small percentage of canisters (14%) may have contained low levels of VOCs when shipped. The laboratory indicated that the most common detections that required re-cleaning included ethanol, acetone, 2-butanone, and carbon disulfide. These constituents were not the primary focus of the investigation. Trip blanks also provide an additional monitor of canister cleanliness.

6.7.2 SUMMARY OF ADDITION OF DATA QUALIFIERS

Qualifiers assigned by the laboratory were unchanged after data validation. Additional qualifiers were assigned to specific data as a result of the data validation review. Additional qualifiers are tabulated in Appendix H, and summarized as follows:

- R qualifiers were added to all chemical analysis for the following samples for which the laboratory oxygen result was greater than 21%. These samples are listed below and are discussed in more detail in Section 6.7.3:

    - CHI1-SS1, 032205; CHI4-SS1, 032205; CHI4-SS2, 032205; HOO3-SS1, 032305; HOO3-SS2, 032305; VW130 (20), 040505;

- R qualifiers were added to all chemical analysis for samples VW-96(35) 032405 HOO1-SS1, 032305; and HOO1-SS2, 032305 due to a difference in canister vacuum ($\geq$ 5 in-Hg) between shipment from the field and arrival at the lab.

- In accordance with EPA (1999), U qualifiers were added to sample concentrations as a result of the presence of detectable VOC concentrations in trip blanks (m,p-xylene detected at 2.8 μg/m^3 in SDG 4361A; toluene, ethylbenzene, m,p-xylene, o-xylene in SDG 0504234A; methylene chloride and carbon disulfide in SDG 4102A; m,p xylene, o-xylene, 1,2,4-trimethylbenzene, 4-ethyltoluene in SDG 4282) and one equipment blank (acetone detected at 13 μg/m^3). Sample concentrations up to five times the blank concentration were U-qualified. For

Trihydro

common laboratory solvents (e.g., acetone), concentrations of up to ten times the blank concentration were U qualified. The U qualifications affected approximately 0.2% of the investigative data. The additional U qualified data are tabulated in Appendix H and the qualifiers are reflected in the data tables in the text.

- J qualifiers were added to sample concentrations that were non-detect and/or detected as a result of laboratory control sample exceedences, laboratory duplicate sample exceedences and/or helium intrusion from the sample shroud into the canister exceeding 5%. Many of the J- qualifiers were due to LCS exceedences for constituents that are not the primary focus of this investigation (i.e. they are not potential COPCs as discussion in Section 8.2). Overall, approximately 2% of the data were qualified as estimated concentrations. However, these are still usable for qualitative purposes. The J-qualifiers are tabulated in Appendix H and reflected in the data tables.

- Some naphthalene data were J qualified either because the associated LCS mixture did not contain naphthalene or as a result of the field test described in Section 6.5.3.1. Where LCS mixtures contained naphthalene, recoveries were consistent and approached 100%. Additional evidence of accuracy specific to naphthalene analysis is the recovery of the surrogate 4-bromofluorobenzene which was added to every sample analyzed. This surrogate has the highest boiling point of those used in this study, and elutes more closely in time to naphthalene than the other method-required surrogates. The surrogate recoveries were also consistent and typically ranged from 90 to 110%, providing additional confidence in the naphthalene results. Therefore, the lack of some LCS results does not adversely affect the utility of the naphthalene data; however, the addition of J qualifiers is procedural and consistent with data validation guidelines. As discussed in Section 6.5.3.1, naphthalene detection limits (23 $\mu g/m^3$) even with a negative bias of two (46 $\mu g/m^3$) are well below the relevant screening level (300 $\mu g/m^3$). Therefore, the naphthalene data are fit for the purpose of the investigation.

6.7.3 SUMMARY OF RESAMPLING EVENTS

Five of the six locations where initial samples were R-qualified as a result of oxygen exceeding 21% were resampled in May 2005 to provide valid data for those locations. The resampling was conducted for both TO-15 and ASTM D-1945. The sixth location, CHI1-SS1, was not resampled because in the companion sample (CHI1-SS2), oxygen values measured by the lab showed good agreement with field data. TO-15 and ASTM D-1945 data from companion soil-gas probe, CHI1-SS2, were used to assess CHI1. Three locations (HOO1-SS1, HOO1-SS2 and VW-96(35)) that were R-qualified as a result of canister pressure differences between shipment from field and arrival at the laboratory were also resampled in May 2005. The original samples had pressure differences greater than the ATL guidance of 5.0 inches of mercury.

Additionally, the following locations were resampled in May 2005 as a precautionary measure due to discrepancy between field and laboratory oxygen measurements or because the canister pressure readings taken after sample collection and arrival at the laboratory differed by more than 4 inches of mercury in the initial samples:

- OHI5-SS1

- OHI5-SS2

- HOO16-SS1

- HOO16-SS2

- VW130(40)

- VW96(30)

- VW96(55)

Review of the laboratory data and procedures demonstrated that the QC results met the method specifications. Therefore, the samples were concluded to be representative. The original samples were also validated; therefore these seven locations have two validated data sets.

6.7.4   RESULTS OF CROSS-VALIDATION

The following SDGs were validated by both Trihydro and GeoSyntec:

- ATL Work Order # 0505080B (ASTM D 1945 analyses)

- ATL Work Order # 0503590C (ASTM D 1945 analyses)

- ATL Work Order # 0503519B (TO-15 analyses)

- ATL Work Order # 0504102A (TO-15 analyses)

- ATL Work Order # 0504140A (TO-15 analyses)

- Lancaster Work Order # HVN 26 (8270C, BNA, moisture)

Validation results from Trihydro and GeoSyntec were in agreement.

6.7.5 OVERALL ASSESSMENT OF DATA QUALITY

The data presented in appendices E through I are considered valid for the purposes of this study and meet the data quality objectives, with the following caveats. The J-qualified data should be used with caution. The R-qualified data should not be used. Assessment of PARCC criteria is described below.

Precision was evaluated by laboratory duplicates, of investigative and laboratory control samples. This resulted in occasional qualification of data as identified in Appendix H. Overall, precision is therefore considered acceptable.

Accuracy was evaluated by known concentration (initial and continuing calibration, surrogate compounds added to samples during analysis, laboratory control samples, MS/MSD samples) and calculating the percent recovery (%R). This resulted in occasional data qualification as identified in Appendix H; however, overall accuracy is considered acceptable.

Representativeness was evaluated:

- in the field – by examining field parameters collected during sample purging, and by evaluating the sampling procedure by drawing a sample of known concentration through the sampling train and comparing the analytical results against the known concentration; and

- in the laboratory – by evaluating instrument performance checks, initial and continuing calibration, laboratory blanks, internal standards, sample homogenization.

This resulted in occasional data qualification as described in Section 6.7.2. Naphthalene and other similar molecular weight compounds may be biased low by up to a factor of 2, as described in Section 6.5.3.2. However, overall representativeness is considered acceptable, provided that this uncertainty is carried through the evaluation. The sampling effort was designed for collection of representative samples. Sampling design is described in Section 4

Completeness was evaluated by calculating the percentage of the number of valid data points that should have been collected. Only one location, CH11, had a sample that was invalidated and was not resampled. Other locations were scheduled for sample collection but samples were not collected due to low permeability or flooding of the sample point, making vapor sample collection impractical. (These locations were all on the west end of town, outside the plume area). The total number of individual sample events (including sub-slab, near-slab, and nested well soil-gas and outdoor air sample locations/dates) was 286 and the total number of valid samples was 285. Therefore, the data set is essentially 100% complete.

Trihydro

Comparability was evaluated by checking for consistency in analytical process (e.g., correct method used for all analysis, same analytes analyzed for, same units reported, holding times were met, detection limits are comparable). Comparability was considered acceptable

Trihydro

7.0 SITE CONCEPTUAL MODEL

This study was designed, in part, to test the previous site conceptual model which had concluded that the vapor intrusion pathway from the groundwater table to indoor air is incomplete. Following are elements of this study used to evaluate and update the site conceptual model: geology and hydrogeology under Hooven, extent of the LNAPL/dissolved-contaminant plumes under Hooven; description of natural processes acting upon petroleum hydrocarbon vapors within the vadose zone, and evaluation of a vapor intrusion pathway from the groundwater table to indoor air.

7.1   SITE CONCEPTUAL MODEL

The Town of Hooven and the adjacent former refinery site lie in a glacial valley incised into Ordovician-age shale and partially filled with glacial outwash and fluvial deposits of the Great Miami River (Spieker and Durrell, 1961; Spieker, 1968; Watkins and Spieker, 1971). As described in the boring logs, the surficial fluvio-glacial aquifer ranges from approximately 20 to 100 feet thick (figures 3, 4, 5, and 6) and is composed of dominantly coarse sediment (Appendix B). A clayey-silt layer at the surface in the western portion of Hooven is the only significant exception to the otherwise relatively uniform coarse texture of soils in the unsaturated zone. This layer exists west of Madison Street (Figure 2a) and thickens to at least 10 feet by the western edge of town. This layer serves as an apparent aquiclude and soil-gas probes set within it were often impossible to sample. Groundwater flows from north to south (Figure 7), although episodic runoff tends to flow eastward over the shallow aquiclude before descending towards the groundwater table and joining regional flow. Figure ES-1 shows a diagrammatic, east to west cross section of the subsurface in Hooven, focusing on a generalization of the extent of VOC contamination from both the surface and from petroleum hydrocarbons attributable to the former refinery.

7.1.1   NATURE AND EXTENT OF SITE-RELATED CHEMICALS: GROUNDWATER AND LNAPL

Petroleum hydrocarbon impacts have been recorded under the eastern portion of town (Figure 8). These impacts extend west from Highway 128 to approximately Adams Street and include dissolved-phase compounds and LNAPL; both are presumed to be derived from a plume extending southwestward from the former refinery. The chemistry of these impacts is consistent with an evaporated gasoline and is further discussed in Sections 7.3 and 7.4. The LNAPL impacts exist in a smear zone approximately 8 feet thick near the groundwater table in the eastern side of town and decrease westward to zero on the western side of town (Figure 8) as indicated by Laser Induced Fluorescence logs taken in 1995, and by boring logs recorded in town. A diagrammatic extent of LNAPL and dissolved contaminant impacts is indicated on figures 4, 5, 6 and 8. The smear zone is a vertical thickness of aquifer which contains some

LNAPL saturation. This thickness typically corresponds to the historical high and low groundwater table in the aquifer. LNAPL has a greater affinity for sediment grains than for water.

7.1.2 SUBSURFACE PATHWAYS

VOCs in deep soil-gas may have been derived either from dissolved species in groundwater partitioning into the vapor phase or from LNAPL partitioning into the vapor phase directly. The very low aqueous solubilities of petroleum hydrocarbon species found in the resident LNAPL plume result in higher VOC concentrations in soil-gas immediately above the LNAPL plume than in soil-gas above the dissolved contaminant plume (figures 9-15). The aqueous VOC population has greater lateral mobility than the LNAPL and therefore produces a greater spatial extent of lesser impacts (Figure 8). Once water table-derived VOCs have partitioned into the vapor phase, their primary means of migration is diffusion, driven by a concentration gradient. This migration tends to be almost exclusively vertical and in agreement with the dominant concentration gradient, resulting in a vapor-phase plume with little or no significant lateral spreading from the LNAPL/dissolved contaminant plume footprint. Further support for the limited lateral extent of the vapor-phase plume is that lateral diffusion has been shown to be restricted to distances of just a few meters (Lowell and Eklund, 2004). As in other similar studies (e.g., Roggemans et. al., 2001), upward-migrating petroleum hydrocarbons are shown to biodegrade to undetectable concentrations before reaching the shallow soil-gas (figures 9-15). Because of this degradation, volatile chemicals originating in the LNAPL/dissolved contaminant plume do not reach ground surface and therefore the vapor intrusion pathway to surface receptors for refinery-related chemicals derived from the groundwater table is incomplete. Further discussion is presented in Section 8.5.

7.1.3 SEASONAL VARIATIONS IN SOURCE

In previous investigations, Chevron has conducted soil-gas sampling in nested soil vapor monitoring wells over the LNAPL plume (VW-93, VW-96, and VW-99) at varying times throughout the calendar year (ESE, 1999 and E&E, 2000, Appendix E). Specifically, sampling was conducted in December 1998 during low groundwater conditions and February 1999 during high groundwater conditions to evaluate the effect of water table fluctuations on vapor concentrations. Greater than 1 foot of LNAPL was observed in each of the three wells during the December 1998 event. LNAPL was not observed during the February 1999 event. Vapor concentrations were generally higher during the February 1999 event compared to the December 1998 event (ESE, 1999). However, regardless of the seasonal effects, all of the sampling events show vapor profiles with high concentrations above the plume which rapidly attenuate with decreasing depth below ground surface.

Trihydro

7.1.4 RECEPTORS

Potential off-site receptors of VOCs derived from the dissolved contaminant plume include the residents of Hooven, construction workers, students and faculty at Hooven Elementary School. Exposures are only possible if the vapors migrate through the unsaturated zone to indoor air without being sufficiently attenuated.

7.1.5 BACKGROUND CONCENTRATIONS AND SOURCES

Despite a considerable thickness of the vadose zone showing few or no detections of VOCs at low reporting limits, detectable levels of VOCs were recorded in a number of locations within the shallow soil-gas. Constituent concentrations and the frequency of detection are similar both inside and outside the LNAPL/dissolved contaminant plume. This is consistent with previous soil vapor results (e.g., Trihydro, 2004a). Because VOC movement is diffusion-driven, and diffusion itself is driven by concentration gradients, it is most likely that VOCs detected in shallow soil-gas originated from surficial or near-surface sources. The results of outdoor air samples collected during the study, summarized on Table 8, showed low concentrations of several VOCs, which is expected near urban areas or highways (http://www.epa.gov/ttn/atw/nata/index.html, EPA, 2002a). Occupied dwelling questionnaires (Appendix A) and field notes from sub-slab soil-gas sampling (Appendix C) describe numerous potential sources of VOCs to shallow soil-gas from consumer products.

8.0 PATHWAY ANALYSIS AND INTERPRETATION

The initial step in a risk assessment for the vapor intrusion pathway, is determining whether the migration/exposure pathway is complete. A complete exposure pathway requires a source of volatile compounds, partitioning of the volatile compounds into the vapor phase at the source, and migration of the vapors from source to a point of exposure, within buildings at the ground surface. This investigation included contaminant source characterization, vapor source characterization, and characterization of the potential migration pathway.

Source characterization included the LNAPL and groundwater sampling. Definition of the LNAPL plume area and dissolved contaminant plume area is presented on Figure 8 and described in Section 8.1. The deepest soil vapor samples, analyzed for VOCs and SVOCs, were used in conjunction with theoretical partitioning calculations using Raoult's Law to constrain maximum concentration of constituents in the source zone.

The vapor migration pathway was *primarily* evaluated through sampling the three nested vapor wells within the LNAPL plume area (VW-93, VW-96 and VW-99) and the two additional nests within the dissolved contaminant plume area (VW-127 and VW-128). Evaluation of these data is presented in sections 8.2 through 8.5. In sections 8.2 and 8.3, data is evaluated relative to constituent-specific generic VI screening criteria. In Section 8.4, the vertical profiles of O_2, CO_2, and selected VOCs are evaluated to investigate the role of biodegradation. In Section 8.5, the nest data are used in Dominant Layer Model (DLM) simulations (Johnson et. al., 1999) to evaluate the role of biodegradation in the vapor profiles and to determine site specific attenuation factors for indicator chemicals.

The vapor migration pathway was *secondarily* evaluated through sampling of sub-slab and near-slab probes at 40 locations inside and 33 locations outside the plume and the Hooven Elementary School. Sampling near or beneath homes outside the plume was important for obtaining site-specific information on background concentrations of constituents of interest. Alternate sources of volatile constituents frequently occur (or are ubiquitous) at the surface in developed/urbanized areas (e.g., EPA, 2002b). Detection of constituents in the shallow subsurface above the plume would only be indicative of a complete pathway for vapor migration if 1) data from deep nests indicates a potential for vapors from the plume to migrate to the near subsurface (5-10 ft-bgs) and 2) detected concentrations are greater than those expected due to background. The shallow data are therefore evaluated, relative to concentrations detected outside the plume and to the results of large regional background studies, in Section 8.6.

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8.1   GROUNDWATER DELINEATION

The dissolved contaminant plume was delineated using dissolved VOC concentration data from 17 wells in the unincorporated town of Hooven (Figure 8). Most of the analytical data was derived from samples collected in 2005. Two wells, MW-82D and MW-97D, however, were last sampled for possible constituents commonly found in gasoline (e.g., VOCs and SVOCs) in the late 1990's. These wells did not show impacts and are transverse to the local groundwater gradient from the plume. The detection/absence of several constituents commonly found in gasoline, (benzene, n-hexane, naphthalene, total benzene, toluene, ethylbenzene and xylenes plus 1,2,4- and 1,3,5-trimethylbenzene) were used to delineate the boundary of the dissolved plume. These data indicated a roughly north-south trending boundary which was used to define current "in plume" and "out of plume" portions of town (Figure 8). The north-south plume edge is consistent with previous results and with the general groundwater flow direction (Figure 7).

8.2   COPC SELECTION

Documentation of a complete pathway for constituent vapors to migrate from a contaminant plume to indoor air first requires identification of the constituent in the source media (LNAPL and /or groundwater), or attribution of the chemical to the source through knowledge of the likely chemistry of the source material. Also required is documentation of partitioning into the vapor phase at the source, and documentation of the presence of the constituent along the migration route from depth to the surface. This investigation was designed to collect the data necessary to evaluate pathway completeness at each of these steps for individual constituents. This section describes the process of identifying Constituents of Potential Concern (COPCs), which are those constituents that have a potential to migrate to indoor air. Following the identification of COPCs, the completeness of the migration pathway for each COPC is described in Section 8.3.

8.2.1   COPC SELECTION CRITERIA AND SCREENING RESULTS

The following initial criteria were used to identify volatile Constituents of Potential Concern (COPCs) for the pathway analysis:

1.   The constituent has a screening value in Table 2b of the OSWER Draft VI Guidance ; and

2.   The constituent can be analyzed by Method TO-15; and either

     a.   The constituent was detected in the LNAPL sample collected from MW-96S or was detected in groundwater samples collected in April 2005; or

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b. The constituent was not evaluated in groundwater or LNAPL but is potentially a volatile component of gasoline and was detected in one or more vapor samples from intervals of 20 ft-bgs or greater in those nested soil vapor monitoring wells within the plume (i.e., VW-93, VW-96, VW-99, VW-127, and VW-128).

Table 9 shows the results of the COPC screening process. The first column lists constituents in order of decreasing relative toxicity. The second and third columns indicate whether the constituent was identified in LNAPL and groundwater, respectively. The fourth column reports detection frequency in deep vapor samples (> 20 ft-bgs) from nested soil vapor monitoring wells located over the plume. Note that the deep nested soil vapor monitoring well data set includes 35 samples; twelve with elevated detection limits due to dilution, and 23 samples that were undiluted. As discussed in Section 6.5.3, some of the deeper samples were diluted by the laboratory, prior to analysis. Only two samples (VW-96 (30') and VW-127 (30'); 5x and 2x, respectively) at a depth of less than 35 ft-bgs were diluted.

Based on Table 9 and the criteria described above, the following COPCs screen through for further evaluation:

- Naphthalene

- Benzene

- 1,2,4-Trimethylbenzene

- 1,3,5-Trimethylbenzene

- Ethylbenzene

- n-Propylbenzene

- n-Hexane

- Acetone

- Isopropylbenzene

- Toluene

- 2-Butanone

- m,p-Xylene

- o-Xylene

8.2.2 IDENTIFICATION OF HIGH PRIORITY COPCS

Table 10 provides a comparison of the maximum detected vapor concentration of each COPC identified in Section 8.2.1 in the deep nested soil vapor well data ($\geq$ 20 ft-bgs) with the relevant screening level from Table 2b of the OSWER Draft VI Guidance. The screening levels are based on target risks of 1.E-5 for carcinogenic constituents and a Hazard Quotient of 1 for non carcinogenic constituents. These target risk levels are consistent with OSWER Draft VI Guidance criteria for Environmental Indicator (EI) determinations (p. 9, EPA, 2002b). The screening levels in column five in Table 10 incorporate an attenuation factor of 0.01. As defined by the EPA, this attenuation factor is a conservative, empirically derived value for application to vapor data collected from 5 feet or more beneath a basement or slab (EPA, 2002b). Therefore, according to the OSWER Draft VI Guidance, it is appropriate (and conservative) to apply this factor to data collected from $\geq$ 20 ft-bgs, as is done in Table 10. It should be noted that the maximum concentrations shown in Table 10 generally come from the deepest interval in one of the nested soil vapor monitoring wells in the plume area (i.e., 55-60 ft-bgs).

Column six in Table 10 shows the ratio of the maximum detected concentration to the screening level. These ratios can be used to rank constituents in terms of the potential for exceeding indoor air screening levels. Ratios greater than 1.0 indicate a potential for exceedence. Based on column 6 in Table 10, benzene and n-hexane are the constituents that are most likely to exceed screening levels. These constituents are further addressed in Section 8.5. Naphthalene was not detected in any of the deep nested soil vapor samples. It was evaluated in Table 10 using the most frequently achieved detection limit (23 $\mu g/m^3$) multiplied by two to correct for the Tedlar® bag sampling bias for naphthalene described in Section 6.5.3.1.

The screening exercise was repeated, in accordance with the OSWER Draft VI Guidance, using semi-site specific attenuation factors derived from Figure 3a and used in Table 3b-SG of the same document. These screening levels are presented in column seven in Table 10. By this method, all COPCs have measured concentrations less than screening levels, indicating that these chemicals do not pose a potential health risk. As discussed in Section 8.6, screening values derived from the semi-site specific attenuation factors are also very conservative.

It should be noted that 2,2,4 trimethylpentane, though detected in deep nested soil vapor monitoring wells, is not identified as a COPC. This is because there is no screening level in Table 2b of the OSWER Draft VI Guidance. This constituent is evaluated in Section 8.5.

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8.2.3 EVALUATION OF CONSTITUENTS NOT ON TO-15 LIST

Two additional evaluations were performed to assess whether the TO-15 analyte list included all of the petroleum hydrocarbon constituents that would have the greatest potential to migrate to indoor air at concentrations above the screening values in Table 2b of the OSWER Draft VI Guidance. The first evaluation was the collection of samples for SVOC analysis from the deepest interval at vapor nests VW-93 (60), VW-96 (55) and VW-99 (55). The procedures for this analysis are described in Section 6.2. SVOCs are of relatively low volatility and are therefore not likely to be COPCs in the vapor phase. However, Table 2b of the OSWER Draft VI Guidance does include VI screening levels for some SVOCs. Therefore, the evaluation was conducted to assess whether any SVOCs would potentially exceed the OSWER Draft VI Guidance screening levels.

The analytical results for the SVOC vapor sampling are included in Appendix F. In the three samples, only 2-methyl naphthalene was detected at a reportable concentration (in sample VW-99 (55), at a concentration of 5.6 $\mu g/m^3$). This concentration is an order of magnitude below the indoor air screening level for 2-methylnaphthalene (70 $\mu g/m^3$) in Table 2b of the OSWER Draft VI Guidance. Therefore, no constituents were added to the COPC list, based on the SVOC vapor analyses.

A final check on the COPC list was conducted using Raoult's Law and results of laboratory analysis of the LNAPL sample from MW-96s. Raoult's Law can be used to calculate theoretical maximum source vapor concentrations in equilibrium with a LNAPL. Empirical data on vapor concentrations immediately above a LNAPL generally show lower concentrations than calculated using Raoult's Law. Table 11 illustrates this concept using the LNAPL and deep vapor nest soil-gas data collected in Hooven. For constituents analyzed in both LNAPL and deep soil gas, the measured vapor concentrations are 10 to 30,000 times lower than those calculated using Raoult's Law. For comparison purposes, the highest detected concentrations over the dissolved contaminant plume were also included on Table 11.

Three constituents that are not amenable to TO-15 analysis are evaluated using Raoult's Law and LNAPL data. As shown in Table 11, the calculated maximum deep vapor concentrations for sec-butylbenzene and 2-methylnaphthalene are less than the screening levels in Table 2b of the OSWER Draft VI Guidance using the generic attenuation factor of 0.01. Therefore, these constituents are removed from the COPC list. The theoretical maximum concentration of n-butylbenzene calculated using Raoult's Law and the generic attenuation factor is slightly above (by a factor of 1.5) the screening levels in Table 2b of the OSWER Draft VI Guidance. However, if the semi-site specific attenuation factors from Figure 3a and Table 3b-SG of the same document are applied to these theoretical maxima, all three compounds fall below their respective screening levels and can be justifiably removed from the COPC list.

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8.3 COMPARISON OF DEEP SOIL-GAS CONCENTRATIONS TO OSWER DRAFT VI GUIDANCE LEVELS

Screening values provided in Table 3b-SG of the OSWER Draft VI Guidance were used to determine if any COPCs identified in the deep soil-gas data set posed a potential risk. Consistent with EPA guidance, the screening values selected from Table 3b-SG were based on a target risk of 1.E-5 for carcinogenic constituents and a Hazard Quotient of 1 for non-carcinogenic constituents, using semi-site specific attenuation factors from Figure 3a of the OSWER Draft VI Guidance as described in Question 5(f) (pp. 33-34) of the same document. These attenuation factors account for the depth to contamination and soil type.

The screening values, developed as described above, were then compared to the deep nested soil vapor well data (samples collected from 20 ft-bgs or greater) for constituents identified as COPCs to determine if there were COPCs present in the deep nested soil vapor well data that were over the screening values. The results of the screening process are presented graphically on figures 16, 17, and 18 can be summarized as follows:

1. COPCs in vapor samples collected from nested soil vapor monitoring wells VW-93, VW-96, and VW-99, located over the LNAPL plume (Figure 8), were below the screening values for depths between 20 and 60 ft-bgs for all constituents with the exception of naphthalene in the deepest intervals of VW-96 and VW-99. The values screened were elevated reporting limits multiplied by two to correct for the Tedlar® bag sampling bias for naphthalene described in Section 6.5.3.1. Naphthalene was not detected in these samples nor was it detected in shallower samples from these nests. The shallower samples had reporting limits that were below the screening level.

2. All COPCs in vapor samples collected from nested soil vapor monitoring wells VW-127 and VW-128, located over the dissolved contaminant plume, were below the screening value for all depth intervals.

3. All COPCs in vapor samples collected from nested soil vapor monitoring wells VW-129 and VW-130, located outside of the plume, were below the screening value for all depth intervals.

8.4 VERTICAL PROFILES OF O_2, CO_2 AND SELECT VOCS

Soil-gas samples from the nested soil vapor wells were used to characterize the vertical profiles of O_2, CO_2, benzene, and n-hexane. Note that these locations were not close to any building and the advective influences of building under-pressurization (reference Section 8.5.2) would therefore not affect the contaminant fate and transport at the locations of

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the nested soil vapor monitoring wells. The vertical soil-gas profiles are grouped into three categories, based on the location of the nested probes relative to the extent of site-related chemicals:

1. overlying LNAPL (VW-93, VW-96, and VW-99),

2. overlying only dissolved petroleum hydrocarbons in groundwater (VW-127 and VW-128), and

3. background concentrations in areas outside the LNAPL/dissolved petroleum hydrocarbons in groundwater (VW-129 and VW-130).

The soil-gas data for these locations are summarized on the profiles presented on figures 9 through 15 and on Table 10. The analytical data reports and data validation reports are included as Appendix H. Review of the soil-gas data shows that the concentration of petroleum hydrocarbon vapors are much lower than the linear concentration profile that would be expected from upward vapor diffusion with no biodegradation. Most of the soil-gas concentrations are near or below the detection limit, except directly above the LNAPL/dissolved contaminant plume. Even in these locations, concentrations decrease to essentially zero between the groundwater table at about 60 feet and a depth of about 30 feet below ground surface. This finding strongly suggests that the vapor intrusion pathway is incomplete.

Profiles of concentrations of benzene, n-hexane, O_2, and CO_2 in soil-gas can be used to provide an indication of whether aerobic degradation is significant.

-   For cases where aerobic degradation is significant, the field data will show a depletion of O_2 concentrations with depth that is correlated to a reduction in contaminant concentration and increase in CO_2 concentration (see figures 9 through 11). It is not uncommon to see O_2 concentrations decrease to 1-2% and CO_2 concentrations increase to several percent in areas where aerobic degradation is active (DeVaull et al. 1997). The active zone is sometimes relatively thin compared to the thickness of the unsaturated zone, which causes the vertical profile of concentrations to change significantly compared to the linear profile that is expected when diffusion is the only significant mechanism (Johnson et. al., 1999). This is likely because soil microbes prefer a certain mixture of air to hydrocarbon for optimal degradation, and are less effective if the mixture is too rich or too lean.

-   For cases where aerobic degradation is not significant, the steady-state soil-gas concentration profile due to diffusion will be linear with the highest concentration at the groundwater table and minimum concentration (near zero) at the ground surface, assuming the contaminant source is at the groundwater table and the overlying geology is relatively uniform; see geologic cross sections presented in figures 3 through 6. A large variation in the O_2 and

CO_2 concentrations throughout the vadose zone will not be seen in these cases. In the nested vapor monitoring wells outside the plume area (VW-129 and VW-130; figures 14 and 15), the oxygen concentrations are about 15% throughout most of the vertical profile, which may be attributable to aerobic degradation of naturally occurring organic matter in the shallow soil (root zone), but there is no further O_2 consumption at increased depths.

8.5   MODELED SITE-SPECIFIC ATTENUATION FACTORS

This section provides a discussion of the influence of biodegradation on petroleum hydrocarbon vapor concentrations and sub-surface to indoor air attenuation factors based on mathematical modeling. The data from this study demonstrate that the vapor intrusion pathway is incomplete and that aerobic degradation has a significant influence, which is common for petroleum hydrocarbons in the unsaturated zone. Calculations using mathematical models provide a supporting line of evidence and can help to assess the relative magnitude of the influence of key fate and transport processes.

8.5.1   THEORY

Three primary processes are typically considered in vadose zone fate and transport analysis for the vapor intrusion pathway (Johnson and Ettinger, 1991, Johnson et al, 1999):

- Vapor diffusion resulting from a concentration gradient of volatile constituents in soil-gas;

- Near surface advection caused by pressure gradients resulting from building under-pressurization; and

- Aerobic degradation of petroleum hydrocarbons.

Diffusion tends to be the dominant transport mechanism through much of the vadose zone due to the absence of pressure gradients (except near buildings, as discussed in the next paragraph). For cases where the lateral extent of the contaminant source is large, diffusion will primarily be upward. However, at the edges of the source area, lateral diffusion may also occur to a limited degree (Lowell and Eklund, 2004).

When evaluating the vapor migration into buildings, advection may an important mechanism in the area close to the building foundation (e.g., within 1 m). Buildings may be under slight positive or negative pressure relative to soil-gas that can cause advection out of or into the building, respectively. These pressure gradients can be caused by wind-load

on the side of the building, temperature differences between indoor and outdoor air, or the use of mechanical ventilation (exhaust fans, etc.). With barometric pressure fluctuations, it is also possible for the flow of soil-gas and indoor air to oscillate between inward and outward (Nazaroff, 1988).

Aerobic degradation plays an important role in the reduction of contaminant concentrations of petroleum compounds in the vadose zone (Ostendorf and Kampbell, 1991; Fisher et al., 1996; Fitzpatrick and Fitzgerald, 1996; Roggemans et al., 2001; DeVaull et al., 2002; CA DTSC, 2005). Some of these studies compared measured and modeled indoor air concentrations while others examined biological activity indicators (O_2 and CO_2) compared to VOC concentrations. A summary of the benzene, toluene, ethylbenzene and xylene (BTEX) biodegradation rate constants has been reported by DeVaull, et al. (1997). Note that different petroleum hydrocarbons are expected to degrade at varying rates. Monoaromatic and n-alkane hydrocarbons are readily biodegradable, but the highly branched alkanes (e.g., 2,2,4-trimethylpentane, also known as isooctane) degrade more slowly (Solano-Serena et al., 2004).

8.5.2   BUILDINGS AS POTENTIAL BARRIERS TO BIODEGRADATION

Theoretically, the presence of a building may act as a partial barrier to the entry of oxygen from the atmosphere to the subsurface, which could potentially reduce the extent of biodegradation under a building, as shown schematically on Figure 19. For illustrative purposes only, model simulations for a generic worst case scenario (LNAPL plume with saturated gasoline vapors and sandy lithology) are shown in Figures 19 through 22 (Abreu and Johnson, 2005b, see Table 12 for model input parameters; Abreu and Johnson 2005a). The modeling is not intended to represent the Hooven site specifically. Three cases are shown, for a theoretical maximum source concentration of 200,000 mg/m^3, which represents total VOC vapor concentration in a saturated gasoline vapor. Figures 20 and 21 show simulations of a building with a basement where the only difference between the two cases is the degradation rate (1.8 and 0.18 hr^{-1}). In both cases, the attenuation factor from the source to indoor air is at least 1,000,000 times lower if biodegradation is included vs. if it is not included. Figure 22 shows a slab-on grade simulation with the same inputs as Figure 21. The plots show petroleum hydrocarbon concentrations in red and oxygen concentrations in blue, each expressed as a fraction of the maximum concentration (Co) (i.e., a "relative concentration" or C/Co). Calculated attenuation factors (the ratio of the modeled concentration in indoor air divided by the source concentration) are shown on each figure for two scenarios; including and not including biodegradation. The model results indicate that the attenuation factors for both basements and slab-on-grade would be very similar with no degradation, but all three scenarios show dramatic increases in attenuation when biodegradation is included.

The sub-slab data collected during this study showed O_2 concentrations that were on average 16.7% for properties located over the LNAPL/dissolved contaminant plume and 18.6% for properties to the west. Ranges of sub-slab O_2 concentrations were 12-21% and 15-21% inside and outside of the plume, respectively. These values are consistent with O_2 concentrations in near-slab probes and nested vapor monitoring well samples from locations outside the plume, which are generally all in the range of 15 to 21%. This result demonstrates that there is no significant oxygen shadow under the buildings in Hooven. These finding are supported with both site-specific data and mathematical modeling as two independent lines of evidence.

8.5.3 DOMINANT LAYER MODEL SIMULATIONS

A vapor transport model was used to evaluate the effect of degradation on the VOC migration in conjunction with the soil-vapor profiles. Johnson et al. (1999) presented an analytical model (the Dominant Layer Model [DLM]) for estimating the migration of VOCs to indoor air that includes vadose zone degradation kinetics. In the DLM, the vadose zone is conceptualized as a three-layer, one-dimensional soil column in which first order degradation is assumed to occur within a specified layer between the source of contamination and building foundation or ground surface. The layer where degradation occurs is referenced as the biodegradation zone or "dominant layer".

8.5.3.1   MODEL CALIBRATION AND APPLICATION

The DLM analysis was performed using data from VW-96 and VW-99. These were the only locations with sufficient detections of VOCs (2,2,4-trimethylpentane or isooctane) to provide a representative vertical profile that could be used to calibrate the model (i.e., the model cannot be calibrated without detected VOC concentrations within the vertical profile). For samples with no detectable 2,2,4 trimethylpentane, the detection limit was used as a surrogate during the model fitting, which provides a conservative calibration (i.e., tends to underestimate the rate of degradation).

No building structures exist above VW-96 and VW-99; therefore, model parameters related to building and ventilation characteristics were assigned to represent open ground-surface conditions for the calibration analysis. Under these conditions, subsurface vapor transport is controlled by diffusion only; and there is no component of near-building advection.

The model inputs were selected based on site-specific data or generic default values, as listed in Table 13a. The degradation rate and thickness of the dominant layer were adjusted to calibrate the model to the site-specific data. An

additional set of calculations was performed by changing the model inputs to allow no degradation. This scenario assists in understanding the significance of aerobic biodegradation on the potential for subsurface vapor intrusion to indoor air.

For each nested soil vapor well, the thickness of the dominant layer was selected to be consistent with the interval where O_2 and CO_2 concentrations were above approximately 1%. The values for the depth interval of the dominant layer and the degradation rate constant determined from the model calibration are presented in Table 13b. The degradation rate constant, λ, was adjusted to optimize the match between the measured and modeled vertical profile of 2,2,4 trimethylpentane concentrations. Biodegradation kinetic parameters for benzene and n-hexane were chosen based on values reported in the literature (English and Loehr, 1991; Kampbell and Wilson, 1991; Jin et al., 1994; Moyer et al., 1996; DeVaull et al., 2002; Pasteris et al., 2002; Ostendorf et al., 2000; Hohener et al, 2003), even though higher degradation rates appear to be occurring at the site, based on the number of non-detect values for soil vapor concentrations.

The modeled and measured concentration profiles are illustrated in Figure 25 for VW-96 and VW-99. Benzene is frequently the key chemical of concern for risk-based analysis at petroleum release sites, so benzene data was included in these plots, even though the results of analyses were non-detect. Non-detect values for both 2,2,4 trimethylpentane and benzene are plotted using the reporting limits as surrogates for the concentration, which is conservative because it overestimates the concentrations. These figures indicate that soil vapor concentration profiles may be predicted using the DLM. The predicted soil vapor concentration profiles are two to five orders of magnitude higher than the actual site data which confirms that biodegradation has a significant effect on contaminant migration in the vadose zone at this site. This result occurs even using the most conservative approach for plotting the non-detect values.

8.5.3.2   ATTENUATION FACTORS

The calibrated DLM inputs were used to estimate the vapor intrusion attenuation factor (ratio of predicted indoor air concentration to source soil-gas concentration) for 2,2,4 trimethylpentane and benzene, with adjustments to simulate a building overlying the vertical profile and associated near-building advection. The inputs for the vapor intrusion attenuation factor modeling are listed in Table 14a. The input assumptions for the building characteristics are typical values for basement and slab-on-grade residential properties (EPA, 2003). A range of attenuation factors for benzene and n-hexane was calculated for several reaction rates using the thickness and location of the middle dominant reactive layer determined in the calibration process. The attenuation factors for non-degradation scenarios were also calculated for comparison.

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Attenuation factors are a function of depth, so the calculated attenuation factors are all expressed as a ratio of the indoor air concentration in a hypothetical building divided by the source concentration (i.e., at the groundwater table, a depth of about 55 ft-bgs). The attenuation factors calculated for 2,2,4 trimethylpentane for each nested soil vapor monitoring well are presented in Table 14b, and range from 1.3E-4 without biodegradation to a value about 100 to 10,000 times lower with biodegradation. The attenuation factors for benzene and n-hexane are shown in tables 14c and 14d, respectively. The attenuation factors for benzene and hexane calculated without biodegradation are 1.9E-4 and 4E-4, respectively, and they are at least 10,000 times lower with biodegradation. The difference between the attenuation factors calculated for basement and slab-on-grade scenarios ranges from 10.5% to 37.5% for the range of degradation rates studied, with basement predictions being higher. The difference between the attenuation factors calculated for basement with bare soil and a foundation with crack ratio of 0.005 ranges from 6.7% to 62.7% for the for the range of degradation rates studied, with bare soil scenario predictions being higher.

In summary, these results demonstrate that biodegradation is a major factor controlling the attenuation factor. In contrast, building construction plays a minor role in determining the attenuation factor, given site conditions at Hooven.

The modeled attenuation factors are all several orders of magnitude lower than the generic attenuation factor of 0.01 used in Table 2b of the OSWER Draft VI Guidance. The modeled attenuation factors are also orders of magnitude below the semi-site specific attenuation factors (1.E-3 to 7.E-4) that are derived from Figure 3a and Table 3b-SG of the OSWER Draft VI Guidance. Therefore the screening in Section 8.3 is very conservative. These results show that the vapor intrusion pathway is incomplete.

The wells selected for the dominant layer modeling (VW-96 and VW-99) are located over the LNAPL plume. The area over the dissolved contaminant plume is difficult to model because constituent concentrations are very low or below the laboratory reporting limit. Therefore, it is difficult to evaluate the change in concentration with depth, which is a key input used by the model to calculate attenuation rate. There is evidence that biodegradation is occurring over the dissolved contaminant plume based on the O_2 and CO_2 profiles (Figures 12 and 13) for the nested wells VW-127 and VW-128, but the biodegradation rate here may be lower than over the LNAPL plume due to lower petroleum hydrocarbon constituent concentrations. Regardless of the biodegradation rate, the pathway is incomplete over the dissolved phase plume (in addition to over the LNAPL plume) because, as shown in Figure 17, the low concentration of petroleum hydrocarbon constituent concentrations in soil gas above the dissolved contaminant plume are below the screening values using the semi-site specific attenuation factor, for all depths below 20 ft-bgs. The semi-site specific attenuation factor does not account for biodegradation.

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8.6 COMPARISON OF SHALLOW SOIL-GAS CONCENTRATIONS TO BACKGROUND

Published studies and guidance documents (e.g. NJDEP, 2002; NYDOH, 2005; CA DTSC, 2005) state that many VOCs listed in the OSWER Draft VI Guidance are common at low levels in outdoor and indoor air, even in places away from groundwater or soil contamination. Because buildings exchange air with both the shallow soil gas around their foundations and the outdoors, it is reasonable to expect similar VOC concentrations in the shallow soil gas. In this study, soil gas samples were collected immediately proximal to home foundations (below or beside them) and as expected, VOC concentrations detected in the sub-slab and near-slab samples beneath Hooven homes are consistent with these documents as shown in Table 7. Additionally, VOCs in shallow soil-gas include compounds not found in gasoline and do not appear to show a preferential distribution with respect to the aerial extent of the dissolved contaminant plume. The compound MTBE, which was common in gasoline mixtures more modern than those produced at the Chevron facility, was detected in shallow soil-gas samples, but was not detected in any of the deep soil-gas samples collected directly over the plume. These observations indicate that VOCs in shallow soil-gas are derived from an alternate source or sources (i.e., background).

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9.0 CONCLUSIONS

During March – May 2005, Chevron conducted a comprehensive investigation of the potential for vapor migration from the LNAPL/dissolved contaminant plume beneath Hooven to indoor air. The results are summarized as follows:

1. New wells installed and sampled during this investigation provide additional data and understanding of groundwater flow conditions and the extent of the dissolved contaminant plume beneath the eastern portion of Hooven. Results of the March – May 2005 monitoring support the previous plume delineation and confirm groundwater flow generally to the south.

2. Petroleum hydrocarbon constituents are detected in vapor samples collected from immediately above the LNAPL and dissolved contaminant plume. Concentrations rapidly attenuate with distance above the LNAPL plume. Concentrations above the dissolved plume were low.

3. Soil-gas concentrations of constituents detected in the LNAPL/dissolved contaminant plume are below the semi-site specific screening levels in Table 3b-SG of the OSWER Draft VI Guidance at depths between 20 and 60 ft-bgs in all five nested soil vapor monitoring wells located inside the LNAPL/dissolved contaminant plume area. These data demonstrate that soil vapors are attenuated within a short distance above the groundwater table and do not reach ground surface. In accordance with the OSWER Draft VI Guidance and consistent with the previous risk assessment conducted for the site, the vapor intrusion pathway is incomplete and vapors from the plume do not migrate to indoor air in residences in Hooven.

4. Inside the plume area, oxygen profiles in well nests show soil-gas O_2 concentrations decrease with depth and CO_2 concentrations increase with depth. These profiles are consistent with empirical evidence from other petroleum hydrocarbon sites and mathematical modeling of vertical diffusion with biodegradation. Collectively, the data and theory provide two lines of evidence which demonstrate that biodegradation is the dominant mechanism for attenuation of petroleum hydrocarbon constituents in the deep vadose zone (~30-55 ft-bgs) within the plume footprint.

5. A mathematical model was calibrated to match the site specific constituent profiles (Figure 25). Biodegradation was incorporated in the modeling to match the constituent profiles. The model inputs were either based on site-specific data or selected to be conservative relative to site-specific conditions. The calculated attenuation factors were ≤3.5E-6 for 2,2,4 trimethylpentane, ≤6.2E-8 for benzene, and ≤ 8.5E-8 for n-hexane. These site-specific attenuation factors are orders of magnitude lower than the conservative generic attenuation factor in the OSWER

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Draft VI guidance (1.E-2), as well as the semi-site specific attenuation factors of 1.E-3 to 7.E-4 from Figure 3a of the OSWER Draft VI Guidance. Therefore the COPC screening conducted in Section 8.2, using the generic OSWER Draft VI Guidance attenuation factor (0.01), is an extremely conservative approach for this site. Additionally, use of the semi-site specific attenuation factors from Figure 3a and Table 3b-SG of the OSWER Draft VI Guidance (1.E-3 to 7.E-4) (Section 8.3) is also a very conservative approach for this site.

6. Outside the plume area, there were no elevated concentrations of petroleum hydrocarbons in the deepest soil vapor samples, and vertical profiles of O_2 and CO_2 did not show evidence of significant biodegradation activity. These results are consistent with background conditions and provide a control to the in-plume results, supporting the occurrence of biodegradation above the plume.

7. Soil-gas data from sub-slab and near-slab probes show that constituents commonly found in gasoline *and* constituents not commonly found in gasoline are present at similar low concentrations and at similar frequencies both inside and outside the plume. Published studies and guidance documents (e.g. NJDEP, 2002; NYDOH, 2005; CA DTSC, 2005) state that many VOCs listed in the OSWER Draft VI Guidance are common at low levels in outdoor and indoor air, even in places away from groundwater or soil contamination. Because buildings exchange air with both the outdoors and the shallow soil gas around their foundations, it is reasonable to expect similar VOC concentrations in shallow soil gas. In this study, soil gas samples were collected immediately proximal to home foundations (beneath and beside them). VOC concentrations detected in these samples from near Hooven homes are consistent with the referenced studies. In addition, MTBE, a gasoline additive that was not commonly used until after the Chevron refinery was shut down, was detected in shallow soil-gas samples, but was not detected in any of the deep soil-gas samples collected directly over the plume. Therefore, detected shallow soil vapors are attributed to background conditions related to human activities at the surface.

8. Sub-slab oxygen concentrations in soil-gas are similar inside and outside the plume. Oxygen concentrations range between 12% and 21% (average 16.7%) in sub-slab soil-gas samples from inside the plume. Oxygen concentrations range between 15% and 21% (average 18.6%) in sub-slab soil-gas samples from outside the plume. These oxygen concentrations are sufficient to support active aerobic biodegradation.

These results provide multiple lines-of-evidence that the vapor intrusion pathway is not complete. Because of this finding, several evaluations are not necessary and have not been conducted in detail. These evaluations include comparisons between sub-slab and near-slab soil-gas data, comparisons between soil-gas data from different construction types, comparison of near-slab sample results from the four different sides of the same building structure, and detailed chemical forensic analysis of shallow soil vapor data.

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The investigation results address the EPA comments received in January 2004 as follows:

1. There are two principal basement construction types in Hooven: 1) full basement with concrete pad, and 2) combination concrete/dirt basement and/or dirt crawlspace. However, building construction type does not play a role in exposure to vapors attributable to the LNAPL/dissolved contaminant plume. Vapors from the plume are attenuated to below detectable concentrations at depths more than 30 ft-bgs (figures 16 through 18).

2. EPA had requested that updated toxicity data be used for ethylbenzene and benzene. The screening levels in Table 2b of the OSWER Draft VI Guidance are based on data available in 2002. Subsequently, the EPA has retracted the carcinogenic toxicity data for ethylbenzene (Choudhury, 2003, personal communication). Therefore, the screening value provided in Table 2b for ethylbenzene may be conservatively low.

In summary, the primary result of this investigation is that residents in Hooven do not incur measurable exposure to vapors originating from the plume that has migrated from the former refinery. Additionally, the results of this investigation support a "YE" determination for the Environmental Indicator CA 725 (Human Health Exposure). A "YE" determination indicates human exposures are "under control" with respect to the vapor intrusion pathway in Hooven.

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